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(54) **Process for producing isobutylene polymers having functional terminal end groups.**

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EP 0 279 456 B1

Description

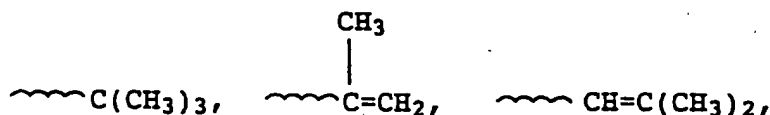
The present invention concerns a process for producing isobutylene polymers having functional terminal end groups at the terminal ends of the polymer chain. More specifically it relates to a process for producing isobutylene polymers in which functional terminal end groups are introduced in a high yield at the terminal ends of the polymer chain during cationic polymerization of one or more cationic polymerizable monomers containing isobutylene, in the presence of a specific initiator and chain transfer agent and a catalyst, and wherein the polymerization is conducted in the presence of a specific mixed solvent.

Polymers having functional end groups are well-known and are useful as starting materials for adhesives, coating materials, sealants, etc. Examples of such polymers include polyalkylene oxides having hydroxyl groups on both ends of the polymer chain, which are referred to as telechelic polymers, used to prepare polyurethanes.

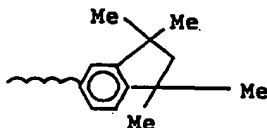
Isobutylene polymers having functional end groups can be produced by the INIFER process, in which isobutylene is cationically polymerized using a halogenated compound, such as 1,4-bis(α -chloroisopropyl) benzene (hereinafter referred to as p-DCC), as an initiator and chain transfer agent and a Lewis acid such as BCl_3 , as a catalyst. That process is described in U.S. Patent No. 4276394.

Isobutylene polymers having chlorine atoms at both ends of the polymer chain obtained by the INIFER process can easily be converted by dehydrochlorination into a polymer having isopropenyl groups at both ends. The polymer having isopropenyl groups can be readily converted by hydroboration to polymers having hydroxyl groups bonded to the primary carbon at each end of the polymer chain.

However, in the polymerization of isobutylene by the INIFER process, as described above, there is a problem that side-reactions tend to occur and considerable amounts of polymers having various kinds of end groups (such as



and



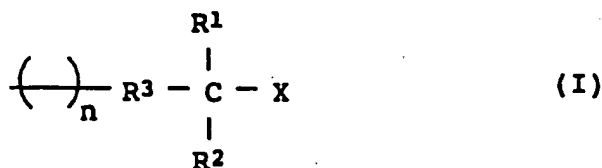
(indanyl group), etc.) are produced, in addition to the desired chlorine-containing ($\sim\text{C}(\text{CH}_3)_2\text{Cl}$) end group. These side reactions can occur under very mild conditions, even when the polymerisation temperature is as low as from -50 to -70°C , and the monomer concentration is as dilute as about 1M.

U.S. 4,611,037 describes an improved process for the production of polymers having halogen end groups from cationically polymerisable monomers using a catalyst system consisting of a metal halide and an organic halide. The organic halide are particular aliphatic halides, are particular aliphatic halogenated hydrocarbons and the metal halide is BX_3 , SnX_4 , TiX_4 , SbX_5 or FeX_3 , wherein X is fluorine, chlorine, bromine or iodine. The concentration of the organic halide and a ratio of metal halide to organic halide fall within specified ranges. Aromatic-substituted or organic halides, such as those which may be used in the present invention, are excluded from the process described in this patent. The hydrocarbon or halogenated hydrocarbon containing an organo nitro compound is not disclosed among the examples of suitable solvents set forth in column 2, lines 25-30.

A primary object of the present invention is to provide a process for producing a polymer in which functional groups, such as halogen atoms, are introduced in a high yield to the ends of the polymer chain prepared using the INIFER process for the cationic polymerization of isobutylene.

The foregoing object can be attained in accordance with the present invention by a process for producing isobutylene polymers having functional end groups from one or more cationic polymerizable monomers containing isobutylene by using:

(A) as an initiator and chain transfer agent, an organic compound having the group represented by the general formula (I):

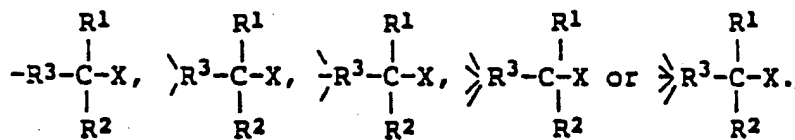


wherein the symbol $\left(\text{---} \right)_n$ designates n-valent bonds meaning that R^3 contains n substituents in addition to the $-\text{CR}^1\text{R}^2\text{X}$ substituent; wherein X represents a halogen atom or an RCOO- group (R represents a hydrogen atom or a monovalent organic group), R^3 represents a $(n+1)$ -valent hydrocarbon group, R^1 and R^2 are a hydrogen atom or a monovalent hydrocarbon group, R^1 and R^2 are taken individually and may be identical or different, but they are not simultaneously a hydrogen atom if R^3 is an aliphatic hydrocarbon group, and n is a positive integer;

(B) as a catalyst, a Lewis acid; and

(C) as a solvent a hydrocarbon or halogenated hydrocarbon containing an organonitro compound, thereby producing isobutylene polymers having functional terminal end groups in which R has the same meaning as above, at its terminal ends.

The group of formula (I) may be illustrated as



According to the process of the present invention, polymers can be obtained in which functional groups, such as halogen atoms, are introduced in high yield at the terminal ends of the polymer chain.

The cationic polymerizable monomer containing isobutylene usable in the present invention is a monomer consisting solely of isobutylene or a mixture of isobutylene and a cationic polymerizable monomer copolymerizable with isobutylene. In the case of using a mixture, mixtures containing not less than 50% (by weight, and hereinafter referred to as the same) of isobutylene in the total monomer are preferred.

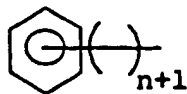
The cationic polymerizable monomer copolymerizable with isobutylene preferably includes those compounds having ethylenically unsaturated bonds with 3 to 12 carbon atoms and can include, for example, olefins, with 3 to 12 carbon atoms, conjugated dienes, vinyl ethers, aromatic vinyl compounds, vinyl silanes or allyl silanes. Among them, olefins or conjugated dienes with 3 to 12 carbon atoms are preferred.

Specific examples of the cationic polymerizable monomer copolymerizable with isobutylene include, for example, propylene, 1-butene, 2-butene, 2-methyl-1-butene, 3-methyl-1-butene, pentene, 4-methyl-1-pentene, hexene, vinyl cyclohexane, butadiene, isoprene, cyclopentadiene, methyl vinyl ether, ethyl vinyl ether, isobutyl vinyl ether, styrene, α -methylstyrene, dimethylstyrene, monochlorostyrene, dichlorostyrene, β -pinene, indene, vinyltrichlorosilane, vinylmethyldichlorosilane, vinyltrimethylchlorosilane, vinyltrimethoxysilane, vinyltrimethylsilane, divinylmethyldichlorosilane, divinylmethoxysilane, divinyltrimethylsilane, 1,3-divinyl-1,1,3,3-tetramethyldisiloxane, trivinylmethyldichlorosilane, tetravinylsilane, allyltrimethylchlorosilane, allyldimethylchlorosilane, allyldimethylmethoxysilane, allyltrimethylsilane, diallyldichlorosilane, diallyldimethoxysilane, diallyldimethylsilane, γ -methacryloyloxypropyl trimethoxysilane, γ -methacryloyloxypropyl methyldimethoxysilane, etc. Among them, preferred are, for example, propylene, 1-butene, 2-butene, styrene, butadiene, isoprene, cyclopentadiene, etc. These cationic polymerizable monomers copolymerizable with isobutylene can be used alone or two or more of them be used together in combination with isobutylene.

In the present invention, the organic compound having the group represented by the general formula (I) is used as the initiator and as the chain transfer agent. In the case where R^1 and R^2 represent monovalent hydrocarbon groups in the general formula (I), it is preferred that they are hydrocarbon groups with 1 to 20 carbon atoms. Some of the hydrogen atoms in the hydrocarbon groups may partially be replaced by other

substituents. Among the hydrocarbon groups, aliphatic hydrocarbon groups with 1 to 12 carbon atoms, such as methyl or ethyl group, are preferred. If both R¹ and R² are hydrogen atoms where R³ is an aliphatic hydrocarbon group, stable carbonium ions are not formed and polymerisation does not progress smoothly.

In the general formula (I), R³ is preferably a hydrocarbon group with 1 to 40 carbon atoms. Some of the hydrogen atoms in the hydrocarbon group may be replaced by other substituents. R³ may be an aromatic hydrocarbon group or aliphatic hydrocarbon group. Examples of R³ can include:



{CH₂}_m

in which n is an integer of 1 to 5, m is an integer of 1 to 10 and $\text{---}(\text{---})_{n+1}$ is as defined above.

In the general formula (I), n is preferably an integer of 1 to 5 and, most preferably, 1 or 2. X represents a halogen atom or an RCOO- group. Examples of the halogen atom can include, for example, fluorine, chlorine, bromine and iodine, with chlorine or bromine being preferred. In the RCOO- group, R is preferably a hydrogen atom or a hydrocarbon group with 1 to 6 carbon atoms and, particularly, an aliphatic hydrocarbon group. Examples of the RCOO- group include, for example, CH₃COO- and C₂H₅COO-.

Examples of the organic compound having the group represented by the general formula (I) include those compounds represented by the general formula (II):

AY_t (II)

where A represents a group having 1 to 4 aromatic rings, Y is a group represented by the general formula (III), attached to an aromatic ring of A:



where R⁴ and R⁵ individually represent a hydrogen atom or a monovalent hydrocarbon group with 1 to 20 carbon atoms, X is a halogen atom or an RCOO- group wherein R is as defined above and t represents an integer of 1 to 6; compounds represented by the general formula (IV):

BZ_k (IV)

wherein B represents a hydrocarbon group with 4 to 40 carbon atoms, Z represents a halogen atom or an RCOO- group (R has the same meaning as described above) attached to a tertiary carbon atom, and k represents an integer of 1 to 4; and oligomers having α-halostyrene units. These compounds may be used alone, or two or more of them may be used in combination.

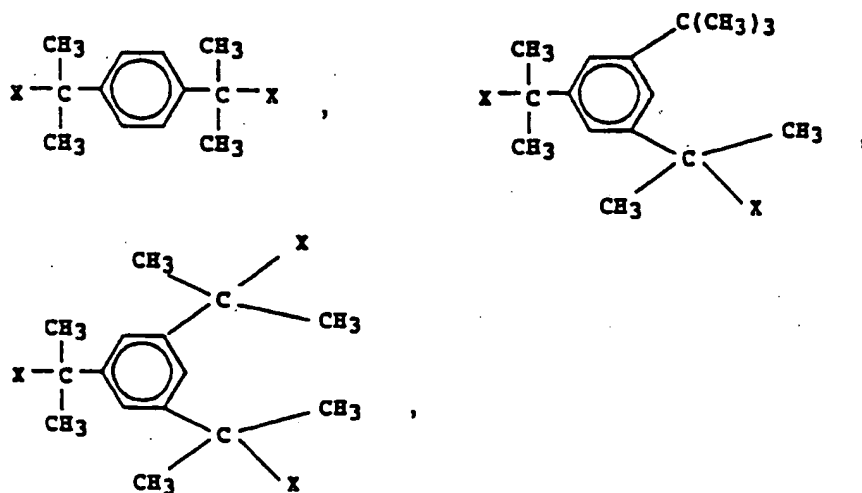
The moiety A which is the group having 1 to 4 aromatic rings in the compound represented by the general formula (II) may be prepared by known procedures, for example, by condensation. Specific examples of such aromatic ring-containing groups include, for example, 1- to 6- valent phenyl, biphenyl, naphthalene, anthracene, phenanthrene, pyrene, ph-(CB₂)_j-ph (where j is an integer from 1 to 10) etc. These groups having aromatic rings may be substituted with aliphatic hydrocarbon groups with 1 to 20 carbon atoms, or those groups having functional groups such as hydroxy, ether and vinyl.

When, on the other hand, the moiety Z in the compound represented by the general formula (IV) is a halogen atom or an RCOO- group attached to the tertiary carbon atom, the moiety B in the general formula (IV) is a hydrocarbon with 4 to 40 carbon atoms and, preferably, aliphatic hydrocarbon group. If the number of carbon atoms is less than 4, a halogen atom or an RCOO- group does not remain bound to the tertiary carbon atom, and such compounds are not suitable for use.

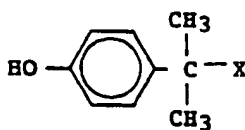
The oligomer containing α -halostyrene units that can be used as the initiator and chain transfer agent can include, for example, an oligomer of α -chlorostyrene or an oligomer prepared by copolymerizing α -chlorostyrene and a monomer copolymerizable therewith.

When a compound having two or more halogen atoms or RCOO- groups is used as the initiator and chain transfer agent in the process according to the present invention, a polymer having functionality on both terminal ends, i.e., so-called telechelic polymer can be obtained. Such polymer is extremely useful.

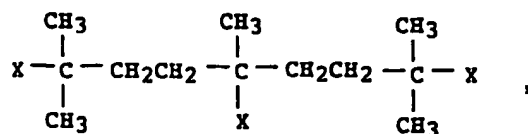
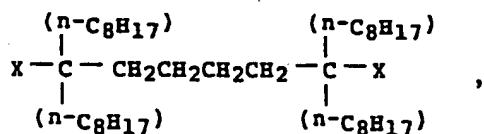
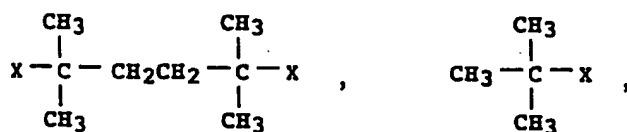
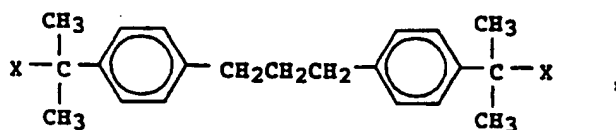
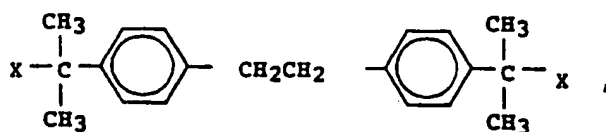
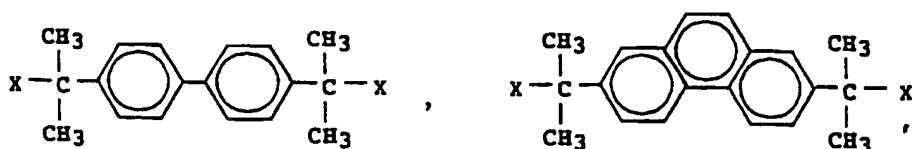
Specific examples of the initiator and chain transfer agent as described above can include, for example,



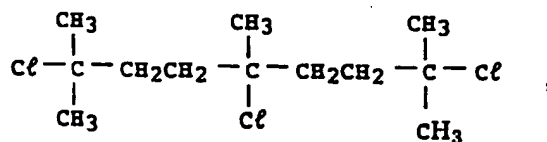
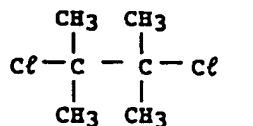
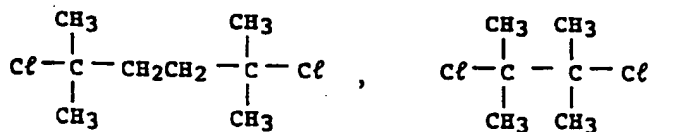
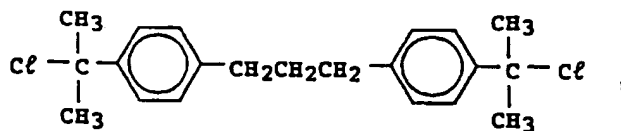
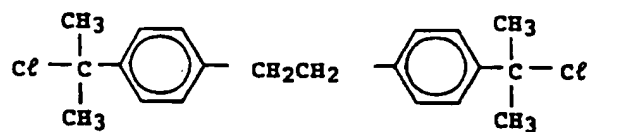
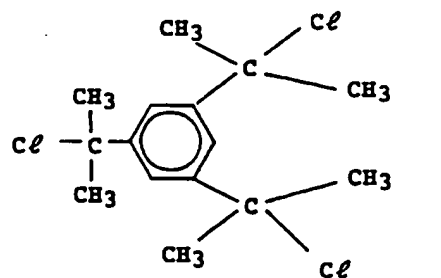
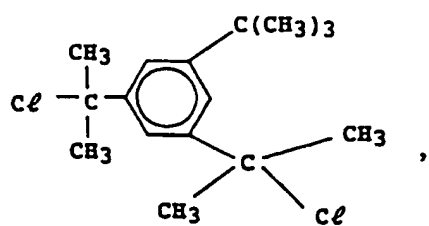
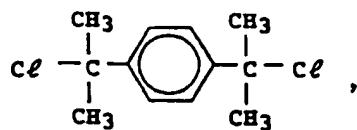
complex salt of



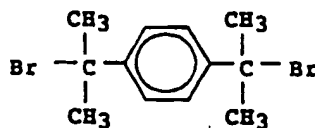
and HCl ,



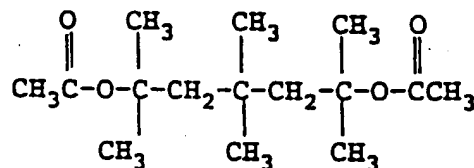
organic compounds containing halogen atoms such as oligomers of α -chlorostyrene or organic compounds containing RCOO- groups. Those preferred among these compounds can include halogen atom-containing organic compounds having $-\text{C}(\text{CH}_3)_2\text{Cl}$ or $-\text{C}(\text{CR}_3)_2\text{Br}$ capable of forming stable carbonium cations, for example,



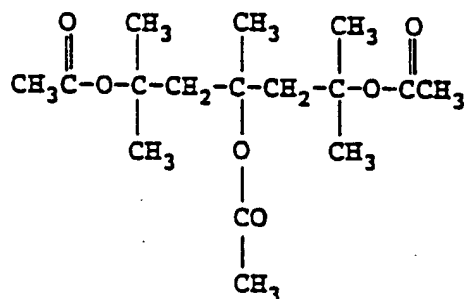
and those compounds in which chlorine atoms are replaced with bromine atoms in the above compounds such as



Further, compounds containing $\text{CH}_3\text{COO-}$ group, such as



and



are also preferred.

These compounds can be the ingredient used as the initiator and as the chain transfer agent and the molecular weight of the polymer can be controlled by the amount used, usually about from 0.01 to 20% by weight and, preferably, from 0.1 to 10% by weight relative to the cationic polymerizable monomer containing isobutylene.

The Lewis acid used in the present invention is the ingredient used as the catalyst. Typical examples of Lewis acids include those compounds represented by MX'_n (in which M represents a metal atom, X' represents a halogen atom and n' represents a positive integer). Examples of MX'_n can include, for example, BCl_3 , AlCl_3 , SmCl_4 , TiCl_4 , VCl_5 , FeCl_3 and BF_3 . Among them, BCl_3 , AlCl_3 , BF_3 , etc. are preferred, with BCl_3 being particularly preferred.

The amount of the Lewis acid is, preferably, from 0.1 to 10 moles and, more preferably, from 2 to 5 moles per mol of the initiator and the chain transfer agent utilized.

In the process of the present invention, a hydrocarbon or a halogenated hydrocarbon containing an organonitro compound is used as the polymerization solvent. Between the hydrocarbons and halogenated hydrocarbons, halogenated hydrocarbons are preferred and, chlorinated hydrocarbons having one or two chlorine atoms are particularly preferred.

Specific examples of the hydrocarbon and halogenated hydrocarbon can include, for example, pentane, hexane, CH_3Cl , $\text{CH}_3\text{CH}_2\text{Cl}$, CH_2Cl_2 , $\text{CH}_2\text{ClCH}_2\text{Cl}$, etc. They may be used alone or as a mixture and, further, may be used together with a small amount of other solvent.

Specific examples of the organonitro compound contained in the hydrocarbon or halogenated hydrocarbon can include, for example, CH_3NO_2 , $\text{CH}_3\text{CH}_2\text{NO}_2$, 1-nitropropan, 2-nitropropane, nitrobenzene, etc., and they may be used in admixture. Among the organonitro compounds those nitrohydrocarbons having one or two nitro groups are preferred.

The ratio of using one or more of the organonitro compound and one or more of the hydrocarbon or halogenated hydrocarbon as the main solvent is preferably from 0.1 to 100 parts by weight, more

preferably, from 0.5 to 20 parts by weight of the organonitro compound based on 100 parts of one or more of the hydrocarbon or halogenated hydrocarbon.

The polymerization method may be batchwise charging solvent, monomer, initiator and chain transfer agent, catalyst, etc. successively into a vessel, or a continuous method of solvent, monomer, initiator and chain transfer agent, catalyst, etc. continuously charged into and taken out of a vessel.

The polymerization temperature is preferably from -10 to -120°C and, more preferably from -20 to -80°C. The polymerization time is preferably from 0.5 to 80 min and more preferably, from 1 to 30 min.

The monomer concentration upon polymerization is, preferably, about from 0.1 to 8M and, more preferably, about from 0.5 to 5M.

The organonitro compounds may be added directly to the main solvent, or added to the solution of the initiator and chain transfer agent or added to the catalyst solution. Further, a catalyst solution prepared from the organonitro compound and the catalyst may be added, and these methods can be employed in combination.

The polymerisation is preferably stopped by the addition of alcohols such as methanol.

The present invention is hereinafter described in greater detail with reference to examples, which are not to be constructed as limiting the scope thereof.

EXAMPLE 1

A stirring blade, a three-way stopcock and a vacuum line were attached to a 1 liter autoclave made of pressure-proof glass and, while evacuating through the vacuum line, the polymerization vessel was dried by heating at 100°C for one hour and, after cooling to the room temperature, the pressure was returned to the normal pressure by opening the three-way stopcock.

Then, while introducing nitrogen from one end of the three-way stopcock, 290 ml of methylene chloride, i.e., a main solvent dried by treatment with calcium hydride was introduced into an autoclave using an injection cylinder. Then, 15 ml of nitromethane dried by treatment with calcium chloride was introduced and, further, 10 ml of methylene chloride solution containing 10 mmol of p-DCC (1,1-bis(α -chloroisopropyl)-benzene) dissolved therein was added.

Then, after connecting, to the three-way stopcock, a liquefied gas sampling tube made of pressure-proof glass attached with a needle valve and containing 40 g of isobutylene dehydrated by passing through a column packed with barium oxide, the polymerization vessel was immersed in a dry ice-acetone bath -70°C and cooled for one hour while stirring its contents. After cooling, the pressure of the inside was reduced via the vacuum line, the needle valve was opened and isobutylene was introduced from the liquefied gas sampling tube made of pressure-proof glass into the polymerization vessel. Then, the pressure was returned to normal pressure by introducing nitrogen from one end of the three-way stopcock and the contents of the polymerization vessel were cooled to -60°C by continuing the cooling for one hour under stirring.

Then, a boron trichloride solution (containing 20 mmol of boron trichloride) was added from the three-way stopcock by an injection cylinder to start the polymerization and, after the elapse of 30 min, methanol previously cooled to lower than -40°C was added to stop the polymerization.

The temperature of the polymerization vessel was returned to the room temperature and the reaction mixture was taken out into a eggplant-shaped flask to remove unreacted isobutylene, methylene chloride, nitromethane and methanol by distillation. After dissolving the residual polymer in 400 ml of n-hexane, the solution was repeatedly washed with water till it became neutral. Then, the n-hexane solution was concentrated to 80 ml and the concentrated solution poured into a one liter of acetone to settle and separate the polymer.

The thus obtained polymer was again dissolved into 400 ml of n-hexane, dried over anhydrous magnesium sulfate, and filtered to remove n-hexane under a reduced pressure to obtain the purified isobutylene polymer.

The yield was calculated from the amount of the resultant polymer produced, \overline{M}_n and $\overline{M}_w/\overline{M}_n$ were determined by GPC, and the end structure was determined by measuring and comparing the intensity of proton resonance signals belonging to each of the structures by the ^1H -NMR (300 MHz) method. The results are shown in Table 1.

EXAMPLES 2-4

Polymers were produced and evaluated in the same manner as in Example 1 excepting for changing the kind and the amount of the organonitro compound as shown in Table 1. The results are shown in Table

1.

EXAMPLES 5-11

- 5 Polymers were produced and evaluated in the same manner as in Example 1 excepting for using 1,1-dichloroethane instead of methylene chloride as the main solvent and changing the kind and the amount of the organonitro compound as shown in Table 2. The results are shown in Table 2.

COMPARATIVE EXAMPLE 1

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 Polymer was produced and evaluated in the same manner as in Example 1 excepting for not using the organonitro compound. The results are shown in Table 1.

COMPARATIVE EXAMPLE 2

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 Polymer was produced in the same manner and evaluated as in Example 5 excepting for not using the organonitro compound. The results are shown in Table 2.

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TABLE 1

Example	Organic compound having nitro group		Yield	Number average Molecular weight (Mn)	molecular weight distribution (Mw/Mn)	Amount of functional group*			
	Kind	Amount (ml)				CH ₃ group	-C-Cl group	Olefin group**	Indanyl
1	CH ₃ NO ₂	15	80	4700	1.8	1.9	0	0	0.1
"	C ₂ H ₅ NO ₂	15	85	4500	1.6	2.0	0	0	0
3	2-nitro-propane	15	85	4800	1.5	2.0	0	0	0
4	Nitro-benzene	15	60	5500	1.8	1.8	0.1	0.1	0.1
Comparative Example 1	-	-	80	9000	3.0	1.1	0.5	0.3	0.3

*: number per one polymer molecule

** : Olefin group means $\begin{array}{c} \text{H} \\ | \\ -\text{C}=\text{CH}_2 \text{ and } \\ | \\ \text{CH}_3 \end{array}$ $\begin{array}{c} \text{CH}_3 \\ | \\ -\text{C}=\text{CH}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$

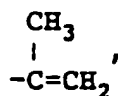
TABLE 2

Example	Organic compound having nitro group		Yield	Number average Molecular weight (Mn)	molecular weight distribution (Mw/Mn)	Amount of functional group*			
	Kind	Amount (ml)				CH ₃ group	-C-Cl group	Olefin group**	Indanyl
5	CH ₃ NO ₂	15	70	4700	1.5	1.7	0.1	0	0.2
6	C ₂ H ₅ NO ₂	15	75	5900	1.8	1.9	0	0	0.1
7	C ₂ H ₅ NO ₂	10	80	5300	1.5	2.0	0	0	0
8	C ₂ H ₅ NO ₂	5	90	5500	1.6	1.9	0	0	0.1
9	1-nitro-propane	15	85	5800	2.0	2.0	0	0	0
10	2-nitro-propane	15	80	5800	1.8	2.0	0	0	0
11	Nitro-benzene	15	50	6000	1.9	1.9	0.1	0	0
Comparative Example 2	-	-	85	5000	2.8	1.2	0.3	0.4	0.4

*: number per one polymer molecule

** : Olefin group means $\begin{array}{c} \text{H} \\ | \\ -\text{C}=\text{CH}_2 \text{ and } \\ | \\ \text{CH}_3 \end{array}$ $\begin{array}{c} \text{H} \\ | \\ -\text{C}=\text{C}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$

As apparent from the results of Table 1 and 2, when polymerization is conducted without using the organonitro compound (Comparative Examples 1, 2), it can be seen that a large amount of



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-CH=C(CH₃)₂ and indanyl groups are present, in addition to the desired -C(CH₃)₂Cl group at the terminal ends of the polymer obtained.

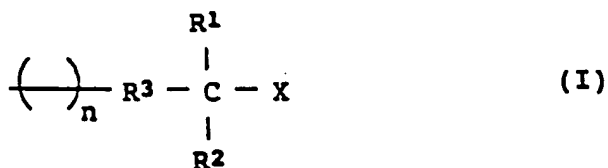
On the other hand, when the polymer having functional terminal end groups is produced by the process according to the present invention, it can be seen that a polymer having the desired -C(CH₃)₂Cl group at high ratio in the terminal ends is obtained in good yields. Sidereactions are suppressed and the molecular weight distribution becomes sharp.

Claims

1. A process for producing isobutylene polymers having functional terminal end groups at the terminal ends of the polymer chain, which comprises polymerizing one or more cationic polymerizable monomers containing isobutylene by using:

(A) as an initiator and chain transfer agent, an organic compound having the group represented by the general formula (I):

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wherein the symbol $\left(\text{---} \right)_n$ designates n-valent bonds meaning that R³ contains n substitutes in addition to the -CR¹R²X substituent; and wherein X represents a halogen atom or an RCOO- group, in which R represents a hydrogen atom or a monovalent organic group, R³ represents a (n+1)-valent hydrocarbon group, R¹ and R² individually represent a hydrogen atom or a monovalent hydrocarbon group, provided that R¹ and R² are not both a hydrogen atom when R³ is an aliphatic hydrocarbon group; and n is a positive integer;

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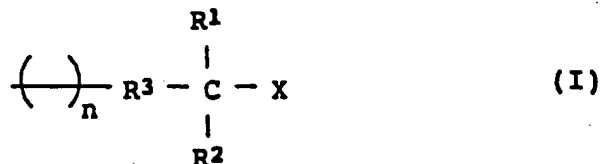
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(B) as a catalyst, a Lewis acid; and

(C) as a solvent a hydrocarbon or halogenated hydrocarbon containing an organonitro compound.

2. A process as defined in claim 1, wherein the organic compound having the group of the general formula (I)

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is a compound of the formula

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AY_t (II)

wherein A represents a group having 1 to 4 aromatic rings, Y is a group of the formula

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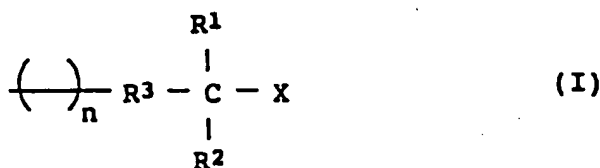
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attached to an aromatic ring of A, wherein R^4 and R^5 taken individually represent a hydrogen atom or monovalent hydrocarbon group with 1 to 20 carbon atoms; X is a halogen atom or a $RCOO-$ group wherein R is defined as in claim 1; and t represents an integer of 1 to 6.

3. A process as defined in claim 1, wherein the organic compound having the group of the general formula (I)

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is a compound of the formula

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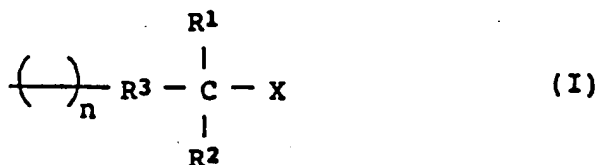
BZ_k (IV)

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wherein B represents a hydrocarbon group with 4 to 40 carbon atoms; Z represents a halogen atom or a $RCOO-$ group attached to a tertiary carbon atom wherein R is as defined in claim 1; and k represents an integer of 1 to 4.

4. A process as defined in claim 1, wherein the organic compound having the group of the general formula (I)

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is an oligomer containing α -halostyrene units.

- 45 5. A process as defined in any one of claims 1 to 4, wherein the organonitro compound is a nitro hydrocarbon having one or two nitro groups.

6. A process as defined in any one of claims 1 to 4, wherein the solvent is a chlorinated hydrocarbon having one or two chlorine atoms and containing a nitrohydrocarbon having one or two nitro groups.

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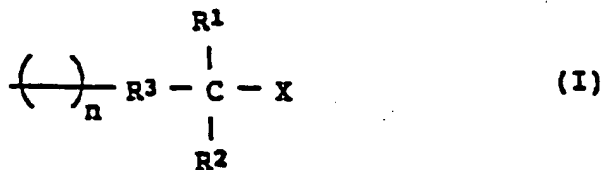
7. A process as defined in any one of claims 1 to 4, wherein the solvent is a solvent in which from 0.1 to 100 parts by weight of a nitrohydrocarbon having one or two nitro groups is added based on 100 parts by weight of a chlorinated hydrocarbon having one or two chlorine atoms.

55 Patentansprüche

1. Verfahren zur Herstellung von Isobutylpolymeren mit funktionellen Endgruppen n am Ende der Polymerkette, umfassend die Polymerisation von einem oder mehreren kationisch polymerisierbaren Mono-

meren, die Isobutylen enthalten, unter Verwendung von:

(A) als Initiator und Kettenübertragungsmittel eine organische Verbindung mit der Gruppe der allgemeinen Formel (I):



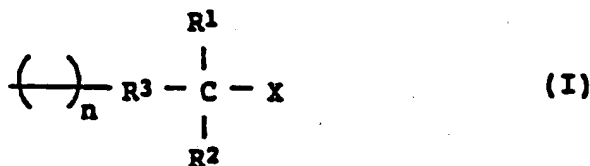
wobei das Symbol $\left(\text{---} \right)_n$ n-wertige Bindungen bezeichnet, was bedeutet, daß R^3 zusätzlich zu dem Substituenten $-\text{CR}^1\text{R}^2\text{X}$ n Substituenten enthält, und wobei X ein Halogenatom oder eine Gruppe RCOO- darstellt, wobei R ein Wasserstoffatom oder eine einwertige organische Gruppe darstellt, R^3 einen $(n+1)$ -wertigen Kohlenwasserstoffrest darstellt, R^1 und R^2 jeweils ein Wasserstoffatom oder einen einwertigen Kohlenwasserstoffrest darstellen, mit der Maßgabe, daß R^1 und R^2 nicht beide ein Wasserstoffatom darstellen, wenn R^3 ein aliphatischer Kohlenwasserstoffrest ist, und n eine positive ganze Zahl ist,

(B) als Katalysator eine Lewis-Säure, und

(C) als Lösungsmittel einen Kohlenwasserstoff oder halogenierten Kohlenwasserstoff, der eine Organonitroverbindung enthält.

2. Verfahren nach Anspruch 1, wobei die organische Verbindung mit der Gruppe der allgemeinen Formel

(I)



eine Verbindung der Formel

AY_l (II)

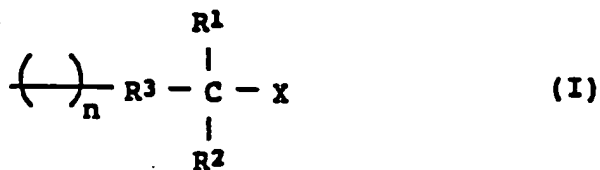
ist, wobei A eine Gruppe mit 1 bis 4 aromatischen Ringen darstellt, Y eine Gruppe der Formel



ist, die an den aromatischen Ring von A gebunden ist, wobei R^4 und R^5 jeweils einzeln ein Wasserstoffatom oder einen einwertigen Kohlenwasserstoffrest mit 1 bis 20 Kohlenstoffatomen darstellen, X ein Halogenatom oder eine Gruppe RCOO- ist, wobei R die in Anspruch 1 angegebene Bedeutung hat, und l eine ganze Zahl von 1 bis 6 darstellt.

3. Verfahren nach Anspruch 1, wobei die organische Verbindung mit der Gruppe der allgemeinen Formel

(I)

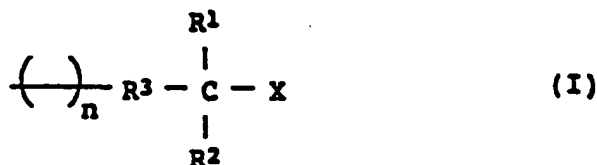


eine Verbindung der Formel



ist, wobei B einen Kohlenwasserstoffrest mit 4 bis 40 Kohlenstoffatomen darstellt, Z ein Halogenatom oder eine Gruppe RCOO- darstellt, die an ein tertiäres Kohlenstoffatom gebunden ist, wobei R die in Anspruch 1 angegebene Bedeutung hat, und k eine ganze Zahl von 1 bis 4 darstellt.

4. Verfahren nach Anspruch 1, wobei die organische Verbindung mit der Gruppe der allgemeinen Formel (I)

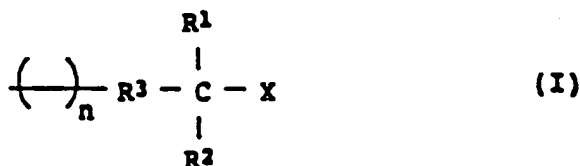


ein α -Halogenstyroleinheiten enthaltendes Oligomer ist.

5. Verfahren nach einem der Ansprüche 1 bis 4, wobei die Organonitroverbindung ein Nitrokohlenwasserstoff mit einer oder zwei Nitrogruppen ist.
6. Verfahren nach einem der Ansprüche 1 bis 4, wobei das Lösungsmittel ein chlorierter Kohlenwasserstoff mit einem oder zwei Chloratomen ist, der einen Nitrokohlenwasserstoff mit einer oder zwei Nitrogruppen enthält.
7. Verfahren nach einem der Ansprüche 1 bis 4, wobei das Lösungsmittel ein Lösungsmittel ist, bei dem 0,1 bis 100 Gew.-Teile eines Nitrokohlenwasserstoffes mit einer oder zwei Nitrogruppen, bezogen auf 100 Gew.-Teile eines chlorierten Kohlenwasserstoffes mit einem oder zwei Chloratomen, zugegeben werden.

Revendications

1. Procédé de production de polymères isobutylène qui ont des groupes terminaux fonctionnels aux extrémités de la chaîne polymère, qui comprend de polymériser un ou plusieurs monomères cationiquement polymérisables contenant de l'isobutylène en utilisant :
- (A) comme un initiateur et agent de transfert de chaîne, un composé organique qui a le groupe représenté par la formule générale (I):



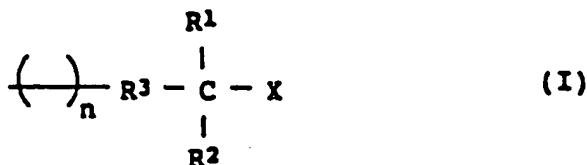
dans laquelle le symbole $\left(\text{---} \right)_n$ r présente une liaison n-valent, c qui signifie que R³ contient n

substituants en plus du substituant $-CR^1R^2X$; t dans laquelle X représente un atome d'halogène ou un groupe $RCOO-$, dans lequel R représente un atome d'hydrogène ou un groupe organique monovalent, R^3 représente un groupe hydrocarbure $(n+1)$ -valent, R^1 et R^2 représentent individuellement un atome d'hydrogène ou un groupe hydrocarbure monovalent, à la condition que R^1 et R^2 ne représentent pas tous les deux un atome d'hydrogène quand R^3 est un groupe hydrocarbure aliphatique; et n est un entier positif;

(B) comme catalyseur est un acide de Lewis, et

(C) comme solvant un hydrocarbure ou un hydrocarbure halogéné contenant un composé organonitro.

2. Procédé selon la revendication 1, dans lequel le composé organique ayant le groupe de formule générale (I):



est un composé de formule :

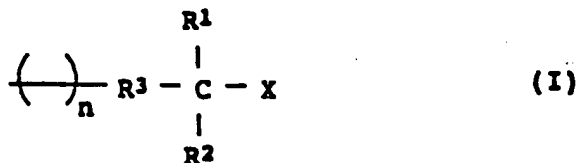


dans laquelle A représente un groupe ayant 1 à 4 cycles aromatiques, Y est un groupe de formule :



fixé à un cycle aromatique de A, dans laquelle R^4 et R^5 représentent individuellement un atome d'hydrogène ou un groupe hydrocarbure monovalent de 1 à 20 atomes de carbone; X est un atome d'halogène ou un groupe $RCOO-$ dans lequel R est défini comme à la revendication 1; et t représente un nombre entier de 1 à 6.

3. Procédé selon la revendication 1, dans lequel le composé organique qui a le groupe de formule générale (I) :

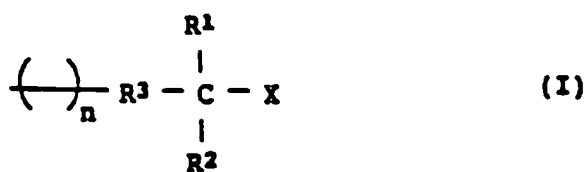


est un composé de formule :



dans laquelle B représente un groupe hydrocarbure de 4 à 40 atomes de carbone; Z r présente un atome d'halogène ou un groupe $RCOO-$ fixé à un atome de carbone tertiaire dans lequel R est tel que défini à la revendication 1; et k représente un entier de 1 à 4.

4. Procédé selon la revendication 1, dans lequel le composé organique qui a le groupe de formule (I):



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est un oligomère contenant des unités α -halostyrène.

5. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le composé organonitro est un hydrocarbure nitré qui a un ou deux groupes nitro.
6. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le solvant est un hydrocarbure chloré qui a 1 ou 2 atomes de chlore et qui contient un hydrocarbure nitro ayant un ou deux groupes nitro.
7. Procédé selon l'une quelconque des revendications 1 à 4, dans lequel le solvant est un solvant dans lequel on ajoute entre 0,1 et 100 parties en poids d'un hydrocarbure nitro ayant un ou deux groupes nitro par rapport à 100 parties en poids d'un hydrocarbure chloré ayant 1 ou 2 atomes de chlore.

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